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CALCULATED PERFORMANCE OF GUN PROPELLANT COMPOSITIONS CONTAINING HIGH NITROGEN INGREDIENTS

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ABSTRACT

The performance of typical ball powder gun propellants has been calculated using a thermodynamic code (the Blake code) and compared with the calculations for HMX and high nitrogen compound mixtures. These ingredients (binder, plasticizer, and high nitrogen compound) were selected for their high enthalpy release and the ability to vary the ratios of ingredients to achieve the desired operating temperature and minimize combustion gas average molecular weight. The mixtures exhibit higher calculated energies than ball powder, and the combustion temperature can be tailored by formulation changes. Comparisons are made between the nitrocellulose/nitroglycerin formulations and the proposed formulations of higher energy.

INTRODUCTION

Gun propellant formulations have been based for many years on nitrocellulose/nitroglycerin (NC/NG) combinations. When a higher energy was sought in this system, it was achieved at the expense of a higher combustion temperature, leading to increased erosion by the hot gases. Both gun and rocket propellants exhibit this direct relationship between an increase in temperature and an increase in available energy.

An inverse relationship exists for both gun and rocket propellants between the average molecular weight of the combustion gases and the energy released. A lower molecular weight corresponds to an increase in the number of moles of gas per unit mass of propellant. Formulation of gun propellants with lower average molecular weight gases is possible while maintaining temperatures in a reasonable operating range.

The NC/NG gun propellants limit the extent to which combustion gas average molecular weight can be decreased by H_2 , since higher energies in these propellants are achieved by replacing C-H bonds with C- ONO_2 or other oxidizers. Gun propellants with lower gas molecular weight, contributed by higher H_2 content, can be devised using azido binders, azido and nitrato plasticizers, nitramines, and high nitrogen tetrazole compounds. Comparisons are made concerning the temperature, energy, and gas molecular weight of these two types of propellant.

DISCUSSION

The ingredients used in the ball powder and the proposed formulations are shown in Table I, along with their densities and heats of formation. The proposed gun propellant ingredients are chosen to maximize enthalpy release while minimizing gas molecular weight. The high nitrogen compounds that are added will decrease gas molecular weight and lower flame temperature with a minimum loss of energy (impetus).

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TABLE I. Gun Propellant Ingredients.

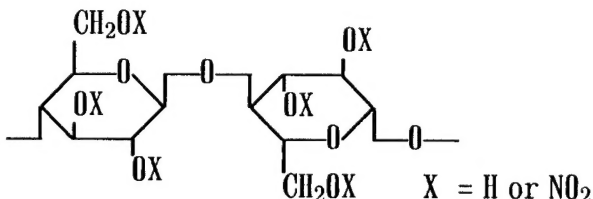
Compound		Density, g/cm ³	ΔHf, cal/g
BAMO/NMMO Copolymer of 3,3-bis(azidomethyl) and 3-nitromethyl-methyl oxetane			
$\left[\begin{array}{c} \text{CH}_2\text{N}_3 \\ \\ -\text{CH}_2\text{CCH}_2\text{O}- \\ \\ \text{CH}_2\text{N}_3 \end{array} \right]_m \left[\begin{array}{c} \text{CH}_2\text{ONO}_2 \\ \\ -\text{CH}_2\text{CCH}_2\text{O}- \\ \\ \text{CH}_3 \end{array} \right]_n$		1.30	330
NC Cellulose trinitrate			
 <p style="text-align: center;">X = H or NO₂</p>		1.55	-617
PGN Polyglycidyl nitrate			
$\left[\begin{array}{c} \text{CH}_2\text{ONO}_2 \\ \\ -\text{CH}_2\text{CHO}- \end{array} \right]_n$		1.45	-57
BTTN 1,2,4-Butanetriol trinitrate			
$\begin{array}{c} \text{ONO}_2 \quad \text{ONO}_2 \\ \quad \\ \text{H}_2\text{C}-\text{CH}-\text{CH}_2-\text{CH}_2 \\ \\ \text{ONO}_2 \end{array}$		1.52	-386
GAP-Azide Azide-terminated glycidyl azide			
$\text{N}_3-\left[\begin{array}{c} \text{CH}_2\text{N}_3 \\ \\ \text{CHCH}_2\text{O} \end{array} \right]_n-\text{CH}_2\text{CHN}_3$		1.27	533

TABLE I. Gun Propellant Ingredients (continued).

Compound		Density, g/cm ³	ΔHf, cal/g
NG	Glyceryl trinitrate		
$ \begin{array}{c} \text{ONO}_2 \quad \text{ONO}_2 \\ \quad \\ \text{H}_2\text{C}-\text{CH}-\text{CH}_2 \\ \\ \text{ONO}_2 \end{array} $		1.60	-400
TMETN	Trimethylolethane trinitrate		
$ \begin{array}{c} \text{CH}_2\text{ONO}_2 \\ \\ \text{H}_3\text{C}-\text{C}-\text{CH}_2\text{ONO}_2 \\ \\ \text{CH}_2\text{ONO}_2 \end{array} $		1.49	-415
HMX	Cyclotetramethylenetetranitramine		
$ \begin{array}{c} \text{NO}_2 \\ \\ \text{H}_2\text{C}-\text{N}-\text{CH}_2 \\ \quad \\ \text{O}_2\text{N}-\text{N} \quad \text{N}-\text{NO}_2 \\ \quad \\ \text{H}_2\text{C}-\text{N}-\text{CH}_2 \\ \\ \text{NO}_2 \end{array} $		1.90	61
ANT	Ammonium 5-nitraminetetrazole		
$ \begin{array}{c} \oplus \\ \text{H}_4\text{N} \quad \text{N} \quad \text{N} \\ \quad \quad \\ \text{N} \quad \ominus \quad \text{CNHNO}_2 \\ \quad \\ \text{N} \quad \text{N} \end{array} $		1.49	222
TAGNAT	Triaminoguanidinium nitraminetetrazole		
$ \begin{array}{c} \oplus \quad \text{HN}-\text{NH}_2 \\ \\ \text{H}_2\text{N}-\text{NH}-\text{C}-\text{NH}-\text{NH}_2 \end{array} \quad \begin{array}{c} \text{N} \quad \text{N} \\ \quad \\ \text{N} \quad \ominus \quad \text{CNHNO}_2 \\ \quad \\ \text{N} \quad \text{N} \end{array} $		1.49	207

BINDERS

Nitrocellulose¹ makes up the major portion of typical ball powder mixtures, usually about 80% by weight. It also provides the bulk of the energy. In the proposed mixtures, the binder is used at about 10% by weight, with the bulk of the energy supplied by the other compounds. Manser² has prepared several variations of azido and nitrate polyoxetanes in recent years (e.g. BAMO/NMMO). Stewart and Golding³ and Willer⁴ have recently prepared polyglycidyl nitrate. Both BAMO/NMMO and PGN are prepared with hydroxy-terminated chains to facilitate polymerization with isocyanate to make urethane bonds. The order of decreasing energy release of the binders is: NC>PGN>BAMO/NMMO.

The calculated energy, flame temperature, and molecular weight of the binders as monopropellants is listed in Table II. Beside each is a listing of the gases produced by combustion, but before expansion and equilibrium shift, which would change gas percentages. NC produces a hot gas mixture (3320 K) with CO and H₂O as the major components, with high average gas molecular weight (25.5). PGN produces a much cooler gas (2344 K) with higher H₂ content and lower gas molecular weight (20.1). BAMO/NMMO combustion is also cooler (2334 K) with substantial N₂ and high H₂ to decrease the molecular weight (17.1).

The BAMO/NMMO and PGN binders, with their low content in the propellants (10%), contribute only a portion of the low temperature properties and low gas molecular weight. This illustrates the limitations imposed by the high content of NC in ball powder mixtures. Additives can lower its temperature only marginally before the ball powder suffers a loss in energy.

TABLE II. Monopropellant Calculations.

Compound	Impetus, J/g	Temp., K	Gas avg. molecular weight	Combustion gas products, %				
BAMO/NMMO	860.7	2334	17.09	H ₂ , 38.8	N ₂ , 39.0	CO, 12.8	CH ₄ , 5.9	
NC	1083.7	3320	25.474	CO, 40.3	H ₂ O, 24.4	CO ₂ , 14.1	N ₂ , 11.9	
PGN	971.3	2344	20.06	CO, 46.2	H ₂ , 27.4	H ₂ O, 13.5	N ₂ , 8.3	
BTTN	1287.8	4047	26.126	H ₂ O, 31.6	CO, 25.0	CO ₂ , 18.3	N ₂ , 15.8	
GAP-Azide	892.7	2339	17.552	H ₂ , 37.1	N ₂ , 37.4	CO, 16.3	CH ₄ , 5.6	
NG	1149.8	4001	29.001	H ₂ O, 28.5	CO ₂ , 27.8	N ₂ , 17.6	CO, 10.5	
TMETN	1255.1	3492	23.134	CO, 36.4	H ₂ O, 27.0	N ₂ , 13.5	H ₂ , 13.4	
HMX	1386.5	4060	24.35	N ₂ , 32.6	CO, 25.1	H ₂ O, 23.2	H ₂ , 8.6	
ANT	1157.6	2932	21.061	N ₂ , 50.0	H ₂ , 22.1	H ₂ O, 13.3	CO, 13.2	
TAGNAT	864.4	2015	19.377	N ₂ , 49.1	H ₂ , 30.3	CO, 12.7	H ₂ O, 3.3	

PLASTICIZERS

Nitrate ester and low molecular weight azide plasticizers are used to enhance the processibility of gun and rocket propellants by lowering viscosity during mixing and increasing the mobility of polymer chains for improved elasticity. These energetic plasticizers also improve the energy release and burning rate of propellants. The order of decreasing chemical energy release for the selected plasticizers is: NG>BTTN>TMETN>GAP-AZIDE.

The plasticizers have different characteristics which make them suitable for different applications. NG as a monopropellant is overoxidized, which would be useful for C-H bond combustion, especially with inert binders and inert fillers. BTTN is less sensitive and less volatile than NG and has residual H₂ to contribute to lower gas molecular weight (26.1, versus 29.0 for NG). TMETN has a higher H₂ content and a lower CO₂ content than NG or BTTN, contributing to a lower gas molecular weight (23.1). This compound produces a favorable energy release in the mixtures while keeping the flame temperature lower than NG or BTTN.

GAP-AZIDE is a relatively new plasticizer, not yet available in large quantities. It creates a substantial cooling effect while releasing large quantities of N₂ and H₂, producing a low gas molecular weight (17.6). This plasticizer is preferred if higher solid energetic nitramine content is desirable, thus lowering the amount of tetrazole filler necessary to lower temperature.

ENERGETIC NITRAMINE

The nitramine HMX provides the major source of enthalpy release for the proposed gun propellants, partly from the weak N-N bonds. HMX as a monopropellant is a high-impetus, high-temperature material. The gas molecular weight (24.4) is reasonably low, with CO₂ at a low level and some H₂ also present. Its high density allows for better processibility with the binder material, lowering the viscosity during mixing.

MOLECULAR WEIGHT DEPRESSANTS

Compounds with high hydrogen and low carbon content contribute to lower gas molecular weight. The high positive heats of formation of some tetrazoles allow for a minimum loss of enthalpy release in compositions where they are used to lower flame temperature. Both ANT⁵ and TAGNAT⁶ decompose as monopropellants to produce half their output gases as N₂. TAGNAT is a more effective compound, producing more H₂ than ANT and lowering temperature more effectively. However, the lower temperature comes with some expected loss of impetus.

COMPOSITIONS

The temperature and energy values are plotted for ball powder^{7,8} and some proposed formulations (Figure 1). The ball powder calculations have energies of about 1000 J/G, and the points plotted (for example, WC-870, WC-872, WC-890) are arranged in a line. Extrapolating a line through some of the points for the proposed propellants suggests a 15% increase in energy is available at the same temperature.

The enhanced energy of the high nitrogen mixtures over ball powder is achieved by lower molecular weight gases (Table III). A typical ball powder generates almost half of its gases as CO, with low amounts of N₂ and H₂ (average gas molecular weight, 23.0). Compositions using BTTN as plasticizer generate substantially more N₂ and have increased amounts of H₂. TMETN formulations are similar, with lower gas molecular weights (average, 20.5). Both TMETN and BTTN are sufficiently energetic to prevent the use of ANT for reducing the temperature to the desired operating range.

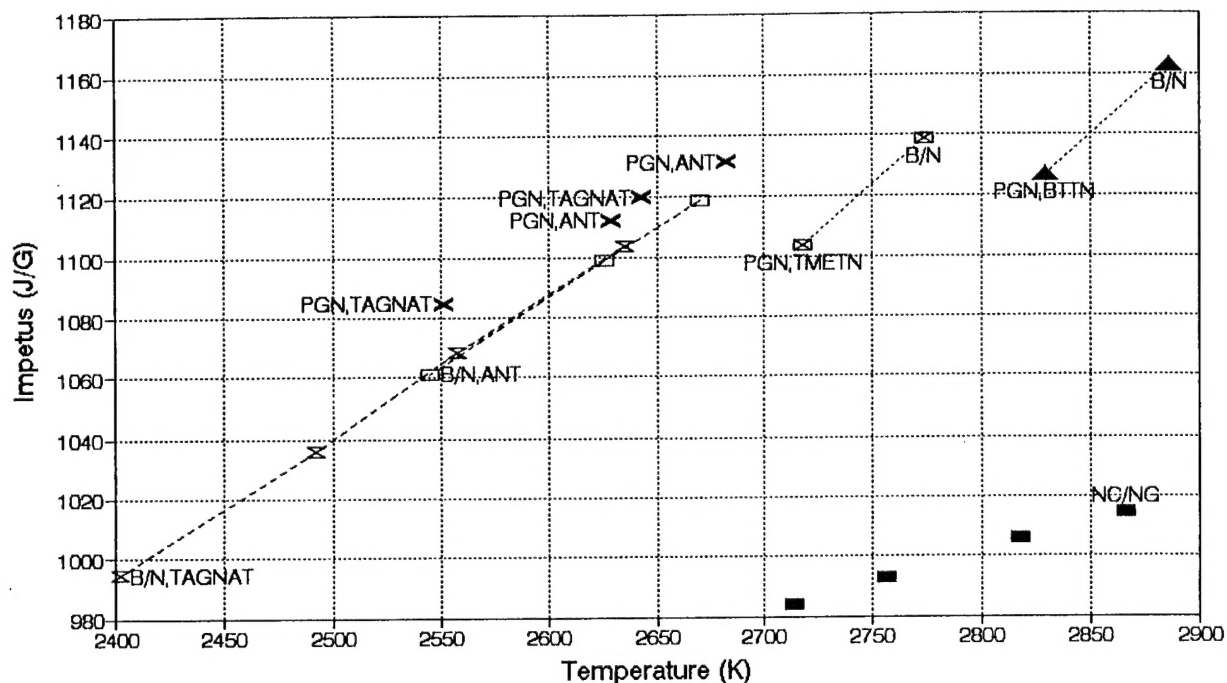


FIGURE 1. Calculations of Gun Propellant Compositions

TABLE III. Results of Sample Calculations.

Composition, %		Temp., K	Impetus, J/g	Gas avg. mol. wt.	Combustion gas products, %			
NC,	80	2817	1006	23.273	CO,	45.8	H ₂ O,	19.7
NG,	11						H ₂ ,	15.6
					N ₂ ,	10.6		
PGN,	10	2643	1120	19.623	CO,	33.6	H ₂ ,	30.9
GAP-Azide	30						N ₂ ,	30.2
HMX,	45							
TAGNAT,	15							
PGN,	10	2718	1104	20.477	N ₂ ,	32.1	CO,	27.0
TMETN,	30						H ₂ ,	24.9
HMX,	15						H ₂ O,	13.5
TAGNAT,	45							
PGN,	10	2829	1127	20.871	N ₂ ,	34.2	CO,	25.0
BTTN,	30						H ₂ ,	22.8
HMX,	10						H ₂ O,	15.3
TAGNAT,	50							

The plasticizer GAP-AZIDE is highly effective in yielding low gas molecular weight (average, 19.8). The gaseous products are almost evenly divided between CO, N₂, and H₂. The mixtures are cool, even with HMX levels of 50% (2635 K), but have energies higher than those of ball powder (e.g., 1103.8 J/G). Both TAGNAT and ANT are effective coolants with GAP-AZIDE, and their cumulative effects with the binders PGN and BAMO/NMMO are apparent in the low temperatures and low gas molecular weights.

CONCLUSIONS

Gun propellants can be formulated to produce flame temperatures in the same range as some typical ball powders, but which have energies 10-15% greater than those of the nitrocellulose/nitroglycerin base propellants. Energetic binders, plasticizers, and tetrazole salts are available which produce large quantities of nitrogen and hydrogen upon combustion. Energetic nitramines provide the enthalpy release for driving the combustion reactions. Combinations of these compounds produce propellants which are high in energy, have moderate flame temperatures, and produce low molecular weight gases.

It should be noted that all calculations were done using the Blake code⁹ at a density of 0.2 g/cm³.

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